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The influence on the corrosion of hydraulic support system of chloride ions in the transmission medium and preventive measures

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Abstract

Hydraulic support is the supporting equipment used in coal mining working face of coal production. Its reliability and life directly affect the quality of supporting underground. The level of chloride ion content in the transmission medium of electro-hydraulic controlling system is an important factor causing fault of hydraulic support. The paper discusses the introducing factors of chloride ion in transmission medium, using adsorption theory and phase membrane theory to explain the corrosion principle and negative effects, and then puts forward the corresponding preventive measures. It has important significance for hydraulic support system to operate safely.

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Keywords: Hydraulic support; Transmission medium; Influence factors; Countermeasures;

1. Introduction

Coal mine underground hydraulic support system is composed of column, oil cylinder, top beam, base, various controlling valves and pipelines and other components. Its main materials are alloy containing silicon, Mn and other elements (such as 16Mn steel and 27SiMn steel, etc). Some precise components are made of stainless steel, which can basically meet the requirements of supporting the coal mine. However,

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in actual production conditions, column, cylinder, passing jack and electro-hydraulic controlling components will be confronted with corrosion, perforation and seal coating scratched off, which will cause hydraulic system channel discharging, pressure pulsing, hydraulic support moving slowly, the carrying capacity of bracket falling down and pipeline corrosion cracking, in extreme cases roof collapse will occur. The study found that about 80% faults are caused by the bad water quality. Most of them are due to high content of chloride ion in the aquifer medium.

Hydraulic support used emulsion pump as the core driving power, hydraulic fluid with high water as working circulated medium. According to MT76-2002 “Hydraulic support (column) with emulsified oil, concentrate and hydraulic fluid with high water”, the hydraulic liquid with high water as production using fluid was mixed by hydraulic transmission medium and water with the ratio of 5:95. The high content of chloride ion in the matching water will cause corrosion of hydraulic support system, resulting in huge losses.

Therefore, the corrosion of water transmission medium of chloride ion in hydraulic support was studied and the corresponding preventive measures were put forward, which made it significant for hydraulic support to operate safely.

1.1. The metal corrosion mechanism of chloride ion

The process of the metal contacting with the surrounding medium, and then interacting and gradually being ruined is called corrosion of the metal. Rust or corrosion is one kind of the metal corrosions. The metal corrosion not only makes the metal material itself damaged in its shape, color and mechanical properties, but also levels down the quality rank, accuracy and sensitivity of the production.

The environment of underground mine production is complex, the air is humid and full of dust and some even contain acid gases. The support column and cylinder which are exposed in air contacting with oxygen, water vapor and contacting medium will produce all sorts of chemical reaction which will leads to corrosion. Such occurrence of corrosion is the main factor of defects of hydraulic support. The contrast diagram about corrosion of stent live column before and after corrosion was shown in Fig. 1

Fig.1 The contrast diagram about corrosion of stent live column before and after corrosion

Ordinary steels have poor corrosion resistance, while stainless steels have good mechanical properties and good corrosion resistance. Xin Ma in Research Institute of Petroleum adopted rotary hitch slice weight-loss method, full immersion weight-loss method and electrochemical method to study the corrosion of 20-carbon steel, 18-8 and 316L stainless steel in alkaline aqueous solution with chloride ions, finding that the existence of chloride ions had an obvious impact on the corrosion rate of carbon steel. When the water contained only 10mg/L chloride ions, the corrosion rate increased rapidly with the increase of the concentration of chloride ions.

For carbon steel and austenitic stainless steel, Cl^- is the root cause of corrosion, and also it plays a strong activation function on the metal passive film. Because of small radius and strong penetration of

chloride ion, it can easily pass through the passive film or tiny pores of coating surface and interact with the metal. When chloride ions permeate into the stent surface and reach a certain concentration, the partial protective film is destroyed and becomes activated state. Under the condition of sufficient oxygen and water, the active surface of hydraulic support body will form a small anode, non-activated coating will form the cathode, and with the increasing concentration of chloride ion in the medium, pitting corrosion potential is decreased, consequently pitting corrosion is prone to happen and accelerate.

Meanwhile, chloride ions have a strong adsorbing ability which can make them be adsorbed by the metal preferentially. The chloride ions will replace O^{2-} when they are adsorbed on the metal surface, and then drain the oxygen from the metal surface. Because oxygen determines the passive state of metals, chloride ions and oxygen fight for adsorption sites on metal surfaces, or even replace passive ions in the process of adsorption in order to form chloride with metal, however, the metal chloride are not stable which leads to the acceleration of corrosion because of the formation of soluble material. Resulting in the destruction of the metal passive state, the Fe^{2+}, Cr^{3+} in the passive film speed up the escape, and then there will be a series of corrosion damage phenomenon. Study found that the passive iron electrode will produce pitting corrosion when the concentration of chloride reaches 3×10^{-4} mole/liter. Experiments showed that in the anodic polarization conditions, the pitting corrosion of metal will happen as long as the containing of chloride ions in medium. Fig. 2 and Fig. 3 are the graphs of occlusion original battery and metal pitting when stainless steel in inflatable NaCl solution, respectively

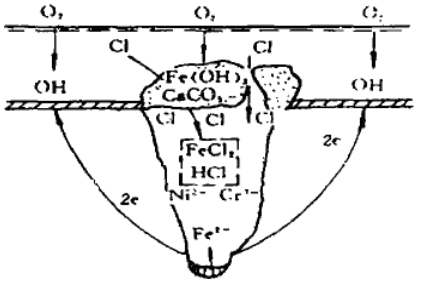

Fig. 2 Schematic diagram of occlusion original battery of stainless steel pitting in inflatable NaCl solution.

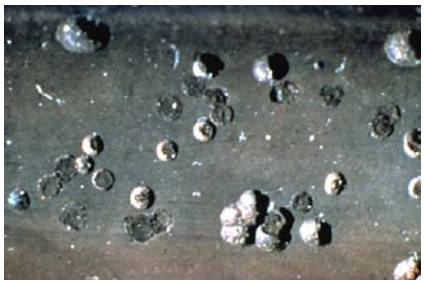

Fig. 3 Diagram of metal pitting

1.2. The corrosive effect of chloride ions on hydraulic support systems

At present, the materials of the hydraulic support and its components are mainly composed of carbon steel and stainless steel. Seen from the bracket corrosive sites in the well, it is more prone to find column pitting, coating off, interior and exterior corrosion of the cylinder, pitting of the stainless steel valves. The corrosive effect of chloride ions in the aqueous medium on the bracket are the followings:

- Effect on carbon steel

Carbon steel is mainly used on column, cylinder and passing jack. Column is the main cover equipment of the fully mechanized hydraulic support, while all kinds of mechanism accident on the column are the main factors which influence the normal operation of hydraulic support. In order to avoid corrosion, support column generally uses external chrome-plating, however when the column contacts with water media with higher levels of chloride ions, the protection function of chrome layer to column will be greatly weakened.

The external chromium coating falls off. When the hydraulic fluid containing high water loops in the support bracket, a small radius of Cl^- can penetrate the surface coating through small cracks to damage

the passive film of internal metal, numerous small primary batteries are formed between the internal metal and surface plating, and then electrochemical reaction occurred. In the interior many small holes are formed, leading to coating off, scratched seal and channeling leakage.

The corrosion of internal cavity. As there is no protective layer inside the cylinder, the chloride irons in the aquifer medium can directly react with wall metal which causes the corrosion in the internal cavity of cylinder. At the same time, the seal components have long-term wear with corrosion point, resulting in leakage and string fluid, so that the quantity of operating fluid in the sub dermal space of upright column reduces. As the support force of hydraulic support is difficult to meet the design requirements, it is bad to roof manage of fully mechanized working face, in this case it will cause a series of problems of safety production. Because of the serious corrosion which is happened between the upright column and the guide sleeve, it is hard to disassemble due to tight thread.

- Corrosion on stainless steel

Cr causes the stainless steel to produce very compact oxide film in oxidized medium, and thus the stainless steel becomes deactivated. This oxide film is the barrier between the steel and the environment, which can deactivate the metal surface in the corrosive medium effectively. The oxide film would weaken stainless steel's corrosion in oxidized medium, so that improve the corrosion resistance of stainless steel.

Guohan Zheng, from Shenyang Chemical Research institute, did massive research work, the experimental results prove that: In 99% acetic acid, infinitesimal amount of Cl^- can destroy the stability of stainless steel. When the Cl^- content in 99% acetic acid increases from 0.0002% to 0.002%, the corrosion rate of stainless steel increases from 0.001mm/a to 1.8mm/a. [3]

In aqueous solution which contains chloride ions, the dissolution will happen on the oxide film of the stainless steel surface, because the chloride ion has priority to be selectively adsorbed on the oxide film to drain the oxygen atoms. Then the chloride ion combines positive ion in the oxide film to form the soluble chloride, resulting in the pore size of 20μm ~ 30μm small pits on the base metal, these small etch pits are the cores of hole corrosion. Among the oxygen, the positive ion oxygen or the positive ion oxidant in medium including chloride ion can urge the eclipsed core to grow into hole, which forms the galvanic battery gradually. The material interchange between inside hole and outside hole becomes more difficult, therefore causes the metal chloride concentrate more in the hole. The chloride hydrolysis makes the medium acidity to further increase, the acidity will further accelerate the anodic dissolution rate, and then high-speed deepening can penetrate metal cross section.

Along with the stainless steel's widespread application in supporting equipment, chloride ion in aqueous medium has more obvious influence on its application, mainly the localized corrosion-hole corrosion. For example, the pock or pitting on electro-hydraulic control valves will cause fluid in the interior valve group to flee and leak. Consequently, the electro-hydraulic control system become malfunctioned, the supporting equipment can not be able to complete prescribed actions. This occasion creates the danger. Moreover, from the localized corrosion, particularly the flaw places subsequently form the big area corrosion, such as blasting or leakage of waste rock smashed the roof coating. [4-6]

2. The introduction factor of chloride irons in transmission medium

In order to control the content of chloride ions in hydraulic support transmission medium, this study selected two representative mine fields in Huainan coal mine area, focusing on the analysis of the various factors which influence the introduction of chloride ion in the transmission medium of hydraulic support. Take the water samples of Liuzhuang mine, Xieqiao mine for the objects of study, simulating the actual conditions of mine water treatment process, adding a certain percentage of flocculants and flocculating agent (the original mine water treatment process using PAC, PAM) for single-factor experiments and mixed experiments in order to study its influence of the content of chloride ion in mine water.

Table 1 shows the characteristics of mine water in different layers of the two mine area. Fig. 2 and Fig. 3 are the charts which illustrate the variation trend of the content of chloride ion in the treated mine water after the use of water treatment agent.

Table 1 Characteristics of water quality in different mine water of different mine areas

WQI(water quality index) / Water sample	Cl^-(mg/L)	SO_4^{2-} (mg/L)	Hardness(mg/L)	PH	Alkalinity (mg/L)
Xieqiao water sample 1#	526.03	624.39	25.93	9.21	353.91
Xieqiao water sample 2#	305.60	437.33	36.30	8.80	995.05
Xieqiao water sample 2#	1095.84	432.27	185.40	8.42	276.97
Liuzhuang mine 171303 working face	78.68	114.04	128.70	8.10	178.54
Liuzhuang mine 121103 working face	638.64	270.11	100.98	8.27	136.48
Liuzhuang hydrological peephole	128.68	300.26	382.26	7.97	182.15

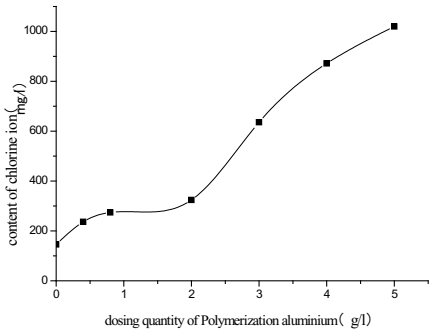

Fig.4 The relationship between dosing quantity of PAC and content of chlorine ion

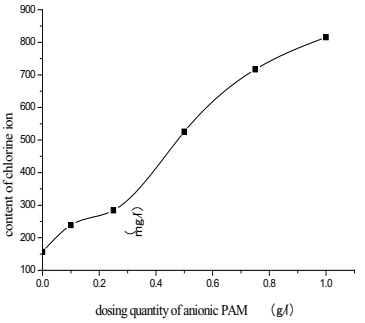

Fig.5 The relationship between dosing quantity of anionic PAM and content of chlor

It can be seen from Table 1 that the content of chloride ion in raw mine water are different in different layers, and there are obvious fluctuations, so the content of chloride ion in raw water can be seen as one of the factors of introducing hydraulic support transmission medium. Fig. 4 and Fig. 5 show that a common water treatment agent with good treatment effect is also another important factor of introducing chloride ion.

3. Solutions

How to deal with liquid water quality match with the influence of electro-hydraulic control system, which must be taken into consideration in mechanism and the root causes. According to the actual

production and laboratory research, we put forward two solving channels of the influence on chloride ions in water.

- Water treatment

According to the characteristics of chloride ions in different water of several mining areas, we choose economic methods for water quality analysis and processing such as sediment filtering method, active carbon adsorption method, water softening method, deionization method, reverse method, ultra filtration method, ultraviolet disinfection method and biological chemical method, and then choose the proper water treatment equipment in order to match the standards. At present the mine water treatment mainly used the precipitation filtering method, water softening and reverse osmosis, etc.

- Add corrosion inhibitors

We can join the corrosion inhibitors if the process conditions permit. The requirements of corrosion inhibitors are to increase the stability of passive film or help the damaged passive film be passivated again. For example, adding 3% of the $NaNO_2$ in 10% of $FeCl_3$ can prevent the pitting corrosion of the 1Cr18Ni9Ti steel chronically.

- The adjustment of emulsion formulation

Making formula adjustment of transmission medium according to liquid water with different contents of chloride ions, the principle of which is to add appropriate complex additives in the formula system according to different water quality index in order to make the emulsion liquid become a "automatic water treatment devices", which produce soluble substances without scale and corrosion through complexing, shielding or reacting.

4. Conclusions

The existence of chloride ion in water medium is the decisive factor of corrosion (especially stainless steel local corrosion). Along with the coal mine mechanization, automation technology unceasing enhancement, more and more application of hydraulic support in mine are used, the impact of mine water quality on electro-hydraulic control system of hydraulic support become more and more obvious. The characteristics of mine water had to be carefully considered and suitable methods of water treatment had to be chosen so as to make full use of the electro-hydraulic control system and realize its potential. Additionally, the good quality of transmission medium would also favor the increase in the life length of the system.

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